

VO_2 : a two-fluid incoherent metal?

M. S. Laad¹, L. Craco² and E. Müller-Hartmann²

¹*Department of Physics, Loughborough University, LE11 3TU, UK*

²*Institut für Theoretische Physik, Universität zu Köln, 77 Zùlpicher Strasse, D-50937 Köln, Germany*
(February 2, 2008)

We present *ab initio* LDA+DMFT results for the many-particle density of states of VO_2 on the metallic side of the strongly first-order (T -driven) insulator-metal transition. In strong contrast to LDA predictions, there is *no* remnant of even correlated Fermi liquid behavior in the correlated metal. Excellent quantitative agreement with published photoemission and X-ray absorption experiments is found in the metallic phase. We argue that the absence of FL-quasiparticles provides a natural explanation for the bad-metallic transport for $T > 340$ K. Based on this agreement, we propose that the I-M transition in VO_2 is an orbital-selective Mott transition, and point out the relevance of orbital resolved one-electron and optical spectroscopy to resolve this outstanding issue.

PACS numbers: 71.28+d, 71.30+h, 72.10-d

Metal-insulator transitions (MIT) in early-transition metal oxides (TMO) are classic examples of correlation-driven Mott-Hubbard transitions [1]. Strong multi-orbital correlations in the real crystal structure (RCS) have turned out to be indispensable for a quantitative description of the MIT in these cases [2].

A detailed understanding of the above cases is still somewhat elusive. In particular, it is still unclear whether the MIT is orbital selective, i.e., whether different orbital-resolved densities-of-states (DOS) are gapped (driving the Mott insulating state) at different values of U, U' (defined below) or whether there is a single (common) Mott transition at a critical interaction strength [3,4]. Conflicting results, even for the same system, and within the same ($d = \infty$) approximation [4] have been obtained, necessitating more work to resolve this issue.

In this communication, we address precisely this issue in vanadium dioxide (VO_2). Using the state-of-the-art LDA+DMFT [5] technique, we first show how excellent quantitative agreement with the full, local one-electron spectral function is achieved using LDA+DMFT(IPT). We then build on this agreement, claiming that the MIT in VO_2 is orbital selective, and represents a concrete, *ab initio* realization of the two-fluid scenario for MIT in strongly correlated systems.

VO_2 shows a spectacular MIT at $T = 340$ K from a low- T monoclinic, Mott insulating phase with spin dimerization along the crystallographic c -axis to a local moment paramagnetic metallic phase. This T -driven MIT has attracted intense scrutiny: because of the additional complication of the antiferroelectric displacement of the VO_6 octahedra in a correlated system, an unambiguous characterization of the MIT (relative importance of Mott-Hubbard versus Peierls dimerization) is somewhat difficult. Various observations have been cited in support of both scenarios [1], and theoretical models detailing the importance of these effects have been proposed [6,7].

One-electron spectroscopies constitute a reliable fingerprint of the changes in the single-particle spectral

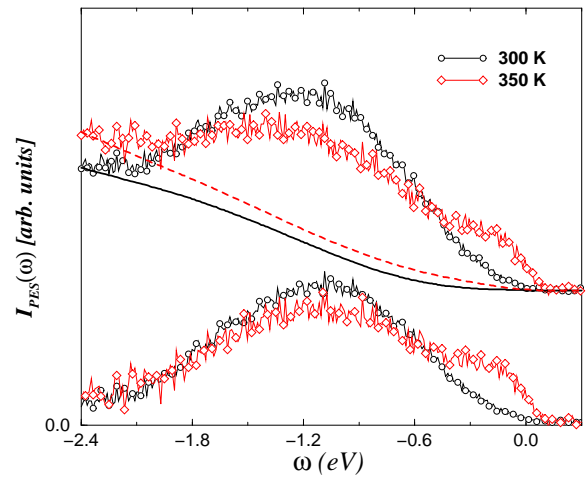


FIG. 1. Photoemission spectrum of VO_2 across the metal-insulator transition, from [11]. Top: raw data; bottom: with the O -2p background subtracted in a way indicated by the region below the solid (300 K) and dashed (350 K) lines.

function (and hence those in the *correlated* electronic structures) across a phase transition. Many papers have studied the MIT in VO_2 by photoelectron- and X-ray absorption spectroscopy (PES and XAS) [8–10]. A perusal of the available literature requires care to pinpoint robust features (weakly dependent on incident photon energy); in what follows, we use only those published data which satisfy this criterion in order to make comparison with theory. Usually, the experiments have been carried out with low incident photon energies (50 – 70 eV) except in Ref. [11] (1200 eV). However, the main features, namely: (i) a broad step-like feature crossing E_F in the R phase, (ii) the “lower Hubbard band” centered at -1 eV, and (iii) the huge O 2p-band contribution from -2 eV, seem to be roughly consistent in all these measurements. Upon subtraction of the O -2p contribution, the corresponding “Vanadium” t_{2g} DOS shows noticeably more spectral weight at lower energies relative to that at -1 eV (Fig. 1).

In this context, great care has to be taken, as, in view of the dynamical transfer of spectral weight over large energy scales characteristic of a correlated system, it is not a priori clear whether the subtracted “background” contains significant intrinsic strong correlation (continuum) contributions. Additional subtraction due to surface contributions to the incoherent part [11] results in noticeably more spectral weight at low energy compared to that at -1.5 eV.

With these caveats, a consistent picture of the changes in the actual electronic structure across the MIT seems to emerge. First, the transition is clearly driven by the dynamical transfer of spectral weight from high to low energy over a large energy scale of $O(2$ eV), characteristic of a Mott-Hubbard scenario. Second, in the metallic (R) phase, there is no semblance of a Fermi liquid-like peak at low energy: rather, the low-energy feature is more-or-less incoherent. This is in good accord with the high resistivity in the (metallic) R phase, as also with the *linear-in- T* dependence without saturation upto 900 K [12]. It is natural to postulate a common electronic scattering mechanism leading to such observations. In the insulating (I) phase, clear evidence of insulating gap formation is visible in PES. From Fig. 3 of Ref. [11], we estimate the gap value $E_G \simeq 0.2 - 0.3$ eV, consistent with that extracted from optical data [13].

The XAS data probe the unoccupied part of the full spectral function, and show a number of interesting features in VO_2 . First, we notice that the XAS intensity is much larger (for $0 \leq \omega \leq 2.0$ eV) than the XPS intensity (for $-2.0 \leq \omega \leq 0$ eV). Second, the broad low-energy “step-like” feature seems actually to be the lower part of the intense feature in XAS pulled below E_F , and is *not* a thermally smeared correlated Fermi liquid resonance. As mentioned above, this fits in nicely with the transport data; in any case, we do not expect a quasicohherent FL scale to survive beyond very low temperatures in a correlated system close to a MI transition.

Beginning with the LDA bandstructure of VO_2 in the monoclinic crystal structure corresponding to the insulating phase [14], with subtraction of terms to avoid double-counting of interactions treated on average by LDA, the one-electron Hamiltonian is,

$$H_{LDA}^{(0)} = \sum_{\mathbf{k}\alpha\beta\sigma} \epsilon_{\alpha\beta}(\mathbf{k}) c_{\mathbf{k}\alpha\sigma}^\dagger c_{\mathbf{k}\beta\sigma} + \sum_{i\alpha\sigma} \epsilon_{i\alpha\sigma}^0 n_{i\alpha\sigma}, \quad (1)$$

where $\epsilon_{i\alpha\sigma}^0 = \epsilon_{i\alpha\sigma} - U(n_{\alpha\bar{\sigma}} - \frac{1}{2}) + \frac{1}{2}\sigma J_H(n_{\alpha\sigma} - 1)$. Here, U, U', J_H are the Coulomb interactions in the t_{2g} shell, and are defined below. The lowest lying xy (in the M notation) band is the most heavily populated, while the $yz \pm zx$ bands are less populated. The bonding-antibonding splitting [14] is clearly visible in the results, which also show that the total bandwidth is about $W \simeq 2.3$ eV, contrary to much smaller previous [7] estimates based on model calculations. Sophisticated LDA

calculations do yield a miniscule, almost zero-gap, Peierls insulator [6], but obviously do not reproduce the Mott insulator. As emphasized by Zylbersteyn *et al.* [7], it is inconceivable that the antiferroelectric distortion alone could open up a charge gap ($E_G \simeq 0.6$ eV), requiring proper incorporation of correlation effects.

Including multi-orbital correlations, the full Hamiltonian is

$$H = H_{LDA}^{(0)} + U \sum_{i\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \sum_{i\alpha\beta\sigma\sigma'} U_{\alpha\beta} n_{i\alpha\sigma} n_{i\beta\sigma'} - J_H \sum_{i\alpha\beta} \mathbf{S}_{i\alpha} \cdot \mathbf{S}_{i\beta}. \quad (2)$$

This multi-orbital Hubbard model is solved using LDA+DMFT(IPT) [3]. Accurate low- and high energy behavior is ensured by requiring strict numerical compliance with the Friedel-Luttinger sum rule (low-energy) and the first three moments of the DOS (high energy). In our approach, the MI transition is driven by the large change in the dynamical spectral weight transfer accompanying small changes in the renormalized antiferroelectric displacement in the *correlated* picture. Hence the transition is of the Mott-Hubbard type, but the antiferroelectric coupling also plays an important role: in fact, it acts like an “external field” in the orbital (t_{2g}) sector. Changes in this external field drives changes in orbital occupation on the one hand, and results in a lowering of the free energy (of the metallic solution) as a function of $\Delta_{\alpha\beta}$, stabilizing the metallic solution at a critical value of $\Delta_{\alpha\beta}$, as found in the calculations. Comparison with data for the insulating state requires incorporation of the c -axis dimerization [7] into our DMFT procedure, and requires extension of the present approach. Hence, we focus only on the metallic state in what follows.

We now compare our theoretical results to experiment, showing how excellent quantitative agreement with the *full* one-electron spectrum in the metallic (R) phase is achieved in this picture. The calculations were done at $T_1 = 150$ K $< T_{MI}$ (I-phase) and $T_2 = 370$ K $> T_{MI}$ (M-phase). We used parameter values identical to those used in Ref. [3]: the LDA bandwidth $W \simeq 2.0$ eV, and interactions specified by $U \simeq 5.0$ eV, $J_H = 1.0$ eV and $U' \simeq (U - 2J_H) = 3.0$ eV for the I-phase. To account for reduction of the effective interaction due to dynamical (selfconsistent) screening processes relevant upon the transition to the M-phase, we use reduced values of $U \simeq 4.6$ eV, $U' \simeq 2.6$ eV in the M-phase, while J_H , being almost unscreened, is kept fixed. As described in Ref. [3], the MIT in our picture results from large changes in dynamical transfer of spectral weight from high- to low energies following small changes in the *renormalized* antiferroelectric distortion in VO_2 .

In Fig. 2, we show the theory-experiment comparison for the total (photoemission + X-ray absorption) intensity, $I_{total}(\omega)$ for the metallic (R) phase. Remarkably,

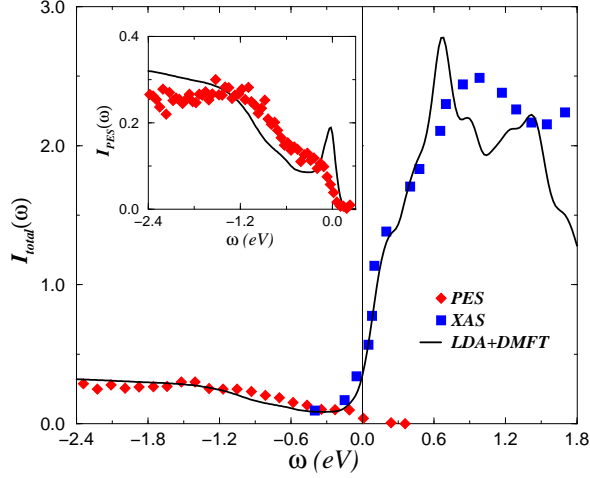


FIG. 2. Comparison of theoretical (LDA +DMFT) result for the total one-electron spectral function in the metallic phase of VO_2 to the experimental results taken from [11] (for PES) and from [9] (for XAS). The inset shows a blow-up of the PES spectrum. The theoretical result is compared with the raw data without subtraction of the O -2p and surface contribution. Subtraction of the surface contribution as in [11] would lead to even better agreement, as explained in the text.

the agreement between theory and experiment in the region $-2.4 \leq \omega \leq 0.8$ eV is excellent. We have not tried to fit the data for $\omega < -2.4$ eV and $\omega > 0.8$ eV because only part of the O -2p and e_g bands of V projected onto the t_{2g} states have been included in our LDA+DMFT calculation. We emphasize that even better agreement could have been obtained if the subtraction of the surface contributions would have been carried out without taking out the O -2p “background” in Fig. 1. This would have had the effect of increasing the weight in the region $-0.3 \leq \omega \leq 0$ eV and decreasing the weight in the region $-1.8 \leq \omega \leq -0.5$ eV [11], further improving the fit.

Several features of the experimental spectra are readily interpreted in the light of the theoretical calculation. First, most of the low-energy spectral weight actually corresponds to (largely incoherent) electronic states close to the minimum of the pseudogap in the spectral function. There is no indication of even a strongly renormalized FL-like resonance. The DOS at $E_F = 0$ eV is drastically reduced compared to the LDA value [14], in excellent agreement with the data, and in full accord with the bad metallic resistivity in the R phase. The lower Hubbard band feature around -1.2 eV is reproduced very well, as is the shoulder-like feature at 0.3 eV in XAS. In [3], we found excellent agreement with the optical effective mass, $m^*/m_b \simeq 3.0$, a value that is also consistent with the observed enhancement of the paramagnetic spin susceptibility in the R phase. Thus, these results represent a quantitatively accurate description of basic spectroscopic and thermodynamic results for the metallic state.

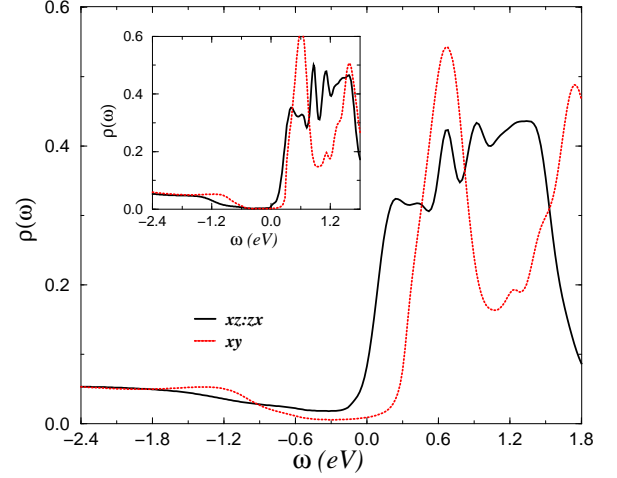


FIG. 3. Orbital-resolved one electron spectral functions for the metallic phase of VO_2 (main frame) and for the insulating phase without spin dimerization (inset). Only the $d_{yz \pm zx}$ orbital DOS crosses E_F in the metallic phase; the d_{xy} DOS still shows Mott-Hubbard insulating features, showing the “two-fluid” character of the MIT in VO_2 .

Armed with this agreement, we proceed to analyze the MIT in VO_2 in more microscopic detail. Fig. 3 shows the orbital-resolved DOS for the metallic phase. Clearly, only the $yz \pm zx$ DOS gives rise to the metallic behavior; the xy orbital DOS is still gapped at a value close to that for the (undimerized, but this is *not* the real lowest state in the I phase) paramagnetic insulating state. This observation, constituting an explicit manifestation of the two-fluid scenario for the Mott transition in VO_2 driven by multi-orbital correlations, is the central result of our analysis. If confirmed by experiment, this result would imply concrete evidence of a multi-orbital correlation driven MIT in VO_2 . We suggest that orbital resolved electron spectroscopies can resolve this general issue of importance for transition-metal oxides. Based on the above analysis, we expect that only the $yz \pm zx$ DOS will cross E_F as T is increased above T_{MI} , while the xy DOS will still show insulating behavior. A detailed analysis of the anisotropic optical spectra across the MI transition driven by strong changes in orbital occupation can also verify the proposed scenario [15].

The above results are also consistent with the large (bad-metallic), linear-in- T resistivity observed in the high- T metallic phase of VO_2 . Indeed, within our DMFT treatment of local (multi-orbital) electronic correlations, the resistivity is expected to show a quadratic temperature dependence for $T < T_{coh}$, a lattice FL coherence scale, but a linear-in- T dependence above T_{coh} up to high temperatures $T^* \simeq J \simeq 4t^2/U \simeq 0.1$ eV [16]. For large U/t , and near the MIT, the resistivity increases way beyond the Mott limit, and increases without saturation. In VO_2 , the MIT occurs at $T_{MI} = 340$ K, which is much

higher than an effective FL coherence scale (which might have been visible if T_{MI} could have been low enough). Hence, the low- T FL-like resistivity is not observed, while the linear-in- T resistivity up to $T^* = 900\text{ K}$ without any hint of saturation can now be identified with the incoherent local (spin-orbital) moment regime of the metallic phase in a multi-band Hubbard model. Using this analogy, we also see that the optical conductivity will be almost completely incoherent in the M phase.

We have not considered the insulating phase with spin dimerization in this communication. To do so requires an explicit consideration of the dynamical effects associated with the c -axis dimerization. This requires a non-trivial extension of DMFT, and we leave it for the future.

In conclusion, we have shown how the two-fluid picture of the Mott transition in VO_2 based on the LDA+DMFT(IPT) yields excellent quantitative agreement with the full one-electron spectrum in the metallic phase. Several features of the bad-metallic transport are also understandable in this picture. Orbital selective one-electron- and optical spectroscopy can confirm/refute this outstanding issue that, in the final analysis, is a manifestation of Mott transitions driven by strong, multi-orbital electronic correlations.

ACKNOWLEDGMENTS

Work carried out (LC) under the auspices of the Sonderforschungsbereich 608 of the Deutsche Forschungsgemeinschaft.

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